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(71) Applicant *(for all designated States except US)*: STEPAN COMPANY [US/US]; 22 West Frontage Road, Northfield, IL 60093 (US).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: FAUNCE, James, A. [US/US]; 705 Pinehurst, North Aurora, IL 60542 (US).

(74) Agent: SCHARFF, Christopher, M.; McAndrews, Held & Malloy, Ltd., 500 West Madison Street, 34th Floor, Chicago, IL 60661 (US).

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Published:
— *with international search report*
— *with amended claims and statement*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: HYDROLYTICALLY STABLE PHTHALATE ESTER LUBRICANTS AND METHOD OF METAL WORKING WITH HYDROLYTICALLY STABLE PHTHALATE ESTERS LUBRICANTS

(57) Abstract: A water-based lubricant is provided that includes a phthalate ester in an amount of about 2 % to about 20 % based on the weight of the final composition and water in an amount of about 60 % to about 93 % based on the weight of the final composition. Also provided are a method of making the water-based lubricant and a method of metalworking using the water-based lubricant.

WO 2005/023967 A1

A PHTHALATE ESTER AS METAL WORKING LUBRICANT

RELATED APPLICATIONS

[0001] [Not Applicable]

FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] [Not Applicable]

[MICROFICHE/COPYRIGHT REFERENCE]

[0003] [Not Applicable]

BACKGROUND OF THE INVENTION

[0004] The metalworking industry requires lubricants in many of its operations. Water-based lubricants are particularly desirable because of the ease of using and disposing of the water base. Adipate esters have also been used as successful lubricants in the metalworking industry. Adipate esters, however, are unstable in water solutions and thus less desirable than water-based lubricants. In the past, it has been determined that esters having groups with steric bulk immediately adjacent the ester group may lend some hydrolytic stability to lubricants. The metalworking industry has gone to utilizing isopropyl and 2-ethylhexyl esters as a source of hydrolytic stability due to the steric bulk of the groups adjacent to the ester linkage. However, there continues to be a need for hydrolytically stable lubricants for use in the metalworking industry.

BRIEF SUMMARY OF THE INVENTION

[0005] The present invention provides a hydrolytically stable phthalate ester lubricant and a method of metalworking with a hydrolytically stable phthalate ester lubricant. The phthalate esters used in the present invention have shown superior hydrolytic stability versus other esters and have shown successful lubrication results in ASTM testing for lubricants.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

[0006] Figure 1 compares the hydrolytic stability of the propoxylated Stepanpol PS-2002 with adipic ester in an acidic system.

[0007] Figure 2 demonstrates the hydrolytic stability of adipate polyol in a basic system.

[0008] Figure 3 demonstrates the hydrolytic stability of the propoxylated Stepanpol PS-2002 in a basic system.

[0009] Figure 4 illustrates the hydrolytic stability of adipate polyol in a KOH system.

[0010] Figure 5 illustrates the hydrolytic stability of the propoxylated Stepanpol PS-2002 in a KOH system.

DETAILED DESCRIPTION OF THE INVENTION

[0011] The phthalate esters that may be used in the lubricant of the present invention include (I) a phthalate polyester-ether polyol, (II) a phthalic anhydride reacted with an equivalent of a fatty alcohol which is then ethoxylated with a variety of moles of ethylene oxide (or propylene oxide), and (III) the amine-neutralized salts of item (II).

[0012] Referring to (I), the phthalate polyester-ether polyol is the reaction product of:

(1) about 2 – 60 % based on the weight of the polyester-ether polyol of phthalic anhydride or phthalic acid;

(2) about 40 - 98 % based on the weight of the polyester-ether polyol of at least one polyol of the formula:

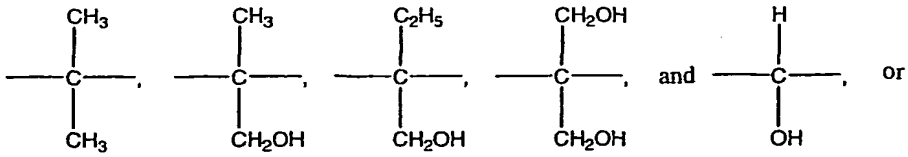
$$HO\text{-}R_1\text{-}OH$$

wherein R_1 represents:

(a) alkylene groups of about 2 to 10 carbon atoms;

(b) $-CH_2\text{-}R_2\text{-}CH_2-$

where R_2 represents:

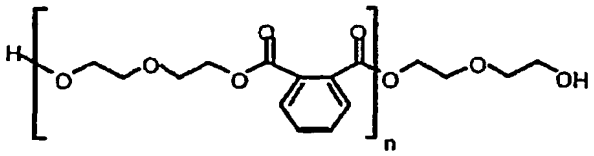


(c) $-(R_3O)_n-R_3-$

where each R_3 independently is an alkylene group of about 2 to about 4 carbon atoms, and n is an integer of from about 1 - 200; and

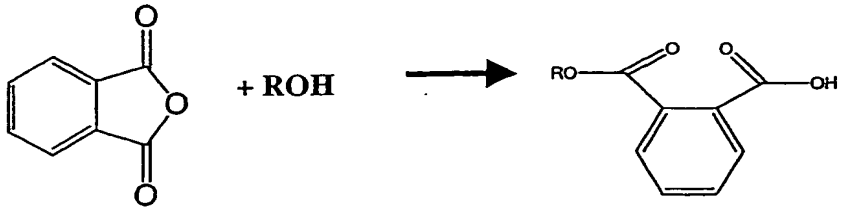
(3) about 10 – 80 % based on the weight of the polyester-ether polyol of an alkoxylating agent.

[0013] A preferred phthalate polyester-ether polyol is a propoxylated diethylene glycol-phthalic anhydride-based polyester polyol. The diethylene glycol-phthalic anhydride-based polyester polyol is sold by the Stepan Company under the tradename Stepanpol PS-2002. Stepanpol PS-2002 has the following structural formula.



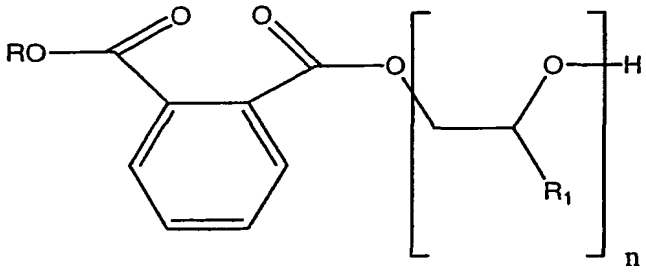
(n ~ 2.0)

[0014] Regarding (II), the phthalic anhydride - fatty alcohol reaction is described as follows.



[0015] where R is C_4 to C_{22}, branched or linear.

[0016] The ethoxylation reaction of the product of the phthalic anhydride - fatty acid reaction proceeds by ethoxylating the product with a variety of moles of ethylene oxide (or propylene oxide or butylene oxide) resulting in the following structure.



where R_1 = H, CH_3, CH_2CH_3, and n = 1-20, preferably 1-10.

[0017] Regarding (III), the amine-neutralized salts of (II) can also be used as the phthalate ester in the present invention. The amines that may be used to accomplish this neutralization include triethanolamine, triethylamine, triethanolamine, monoethanolamine, 2-ethylhexylamine, tallow amine ethoxylates or any other amine in general.

[0018] The stability of the phthalate esters of the present invention was investigated in both acidic and basic conditions and compared to adipic ester, a known lubricant often used in the metalworking industry.

[0019] Figure 1 compares the hydrolytic stability of the propoxylated Stepanpol PS-2002 with adipic ester in an acidic system. Figure 1 depicts the increase in acid value of the adipic ester versus the propoxylated Stepanpol PS-2002 as the acid value increase is indicative of ester breakdown. The results reported in Figure 1 confirm that the phthalate esters of the present invention provide the hydrolytic stability in acidic conditions desirable for lubricants in the metalworking industry.

[0020] Figure 2 and Figure 3 demonstrate the hydrolytic stability of adipate polyol and the propoxylated Stepanpol PS-2002, respectively, in a basic system. Base stability can be observed by measuring the breakdown in molecular weight of the ester over time. Figures 2 and 3 illustrate the breakdown in molecular weight via gel permeation chromotography (GPC) of adipate polyol and the propoxylated Stepanpol PS-2002, respectively, in 0.50M KOH and 0.50M TEA (triethyl amine) by measuring the area percent of the highest molecular weight species in the GPC graph. Figure 2 demonstrates that the area percent of the adipate polyol decreases drastically over time. In contrast, Figure 3 demonstrates that the area percent of the propoxylated Stepanpol PS-2002 does not decrease over the same time period.

[0021] Figure 4 and Figure 5 illustrate the hydrolytic stability of adipate polyol and the propoxylated Stepanpol PS-2002, respectively, in a KOH system. Figures 4 and 5 directly measure the average molecular weight of the systems to demonstrate the respective stability in a basic system. Figure 4 demonstrates that the average molecular weight of the adipate polyol decreases drastically over time. In contrast, Figure 5 demonstrates that the average molecular weight of the propoxylated Stepanpol PS-2002 does not decrease over the same time period, confirming the hydrolytic stability of the pthalate ester

[0022] All of Figures 2, 3, 4, and 5 confirm that the phthalate esters of the present invention provide the hydrolytic stability in basic conditions desirable for lubricants in the metalworking industry.

[0023] The lubricant of the present invention was compared to metalworking industry lubricant standards (isopropyl oleate and 2-ethylhexyl oleate). In particular, the tests run

were a 4-ball wear, Extreme Pressure Pin and Vee, and a Tapping Torque. All tests were run via an ASTM method.

[0024] Table I sets forth the results for the ASTM D-4172 4-ball wear testing.

TABLE I

Product	Wear Diameter (mm)
Stepan MWA-560 HS	0.598
2-ethylhexyl oleate	0.752
isopropyl oleate	0.628

[0025] Table II sets forth the results for the ASTM D-3233 Extreme Pressure Pin and Vee testing.

TABLE II

Product	Failure Load (lbs)
Stepan MWA-560 HS	1000
2-ethylhexyl oleate	1250
isopropyl oleate	1250

[0026] Table III sets forth the results for the ASTM D-5619 Tapping Torque testing.

TABLE III

Product	Efficiency (%)
Stepan MWA-560 HS	96.20
isopropyl oleate	110.28

[0027] The results as set forth in Tables I, II, and III demonstrate that the lubricants of the present invention provide lubricating properties comparable to those of the metalworking industry standards. As such, the lubricants of the present invention may be utilized in any application in the metalworking industry that requires a lubricant such as isopropyloleate or 2-ethylhexyl oleate.

[0028] A typical lubricant formulation useful in the metalworking industry may consist of up to about 90% water, about 5% phthalate ester, and about 5% triethanolamine. Those skilled in the art recognize that many lubricant formulations are maintained as proprietary trade secret information, and that the phthalate esters disclosed above may be utilized as the main lubricating ingredient in those proprietary lubricant formulations. Thus, the present invention includes such lubricant formulations that utilize the phthalate ester as the main lubricating ingredient. In other words, a person skilled in the art may take his or her proprietary formulation and in the place of the prior main lubricating ingredient utilize the phthalate esters to arrive with a lubricant formulation of the present invention. Such proprietary formulation usually include water, the main lubricating ingredient and at least one other ingredient. The at least one other ingredient may be a single ingredient, as described in the formulation above where the at least one other ingredient is triethanolamine, or may include any number of components.

[0029] Typical water-based lubricants presently include water in an amount between about 60% and about 93% by weight of the total composition, preferably about 75 to about 87%, and a main lubricating ingredient in an amount between about 2% and about 20% by weight of the total composition, preferably about 5 to about 10%. The phthalate esters disclosed above may be used as the main lubricating ingredient in such water-based lubricants and in such amounts. Typical water-based lubricants presently further include at least one other ingredient in a total weight of about 2% and about 20% based on the final composition. One typical component of the at least one other ingredients is an amine in an amount of between about 2% and about 10% by weight of the total composition. The amine is typically used to regulate the pH of the lubricant. Thus, the phthalate esters disclosed above can be used in

presently used lubricants by replacing the main lubricating ingredient in those present day lubricants with the disclosed phthalate esters to provide the lubricant of the present invention.

[0030] The phthalate esters disclosed above may also be used as the main lubricating ingredient in such water-based lubricants including this at least one other ingredient.

[0031] The invention has been described with reference to preferred and alternate embodiments. Modifications and alterations will occur to others upon the reading and understanding of the specification. It is intended to include all such modifications and alterations insofar as they come within the scope of the appended claims or equivalents thereof.

[0032] Claims

1. A method of making a water-based lubricant comprising the steps of

providing a phthalate ester;

providing water; and

mixing the phthalate ester and water.

2. The method of claim 1 further comprising the steps of

providing at least one other desirable ingredient; and

mixing the phthalate ester, water and at least one other desirable ingredient.

3. The method of claim 1 wherein the phthalate ester is provided in a amount of about 2% to about 20% based on the weight of the final composition; and

the water is provided in an amount of about 60% to about 93% based on the weight of the final composition.

4. The method of claim 2 wherein

the phthalate ester is provided in a amount of about 2% to about 20% based on the weight of the final composition;

the water is provided in an amount of about 60% to about 93% based on the weight of the final composition; and

the at least one other desirable ingredient is provided in a total amount of about 2% to about 20% based on the weight of the final composition.

5. A water-based lubricant comprising

phthalate ester in an amount of about 2% to about 20% based on the weight of the final composition;

water in an amount of about 60% to about 93% based on the weight of the final composition.

6. The water-based lubricant of claim 5 further comprising

at least one other desirable ingredient in a total amount of about 2% to about 20% based on the weight of the final composition.

7. The water-based lubricant of claim 6 wherein the phthalate ester comprises 5% by weight of the final composition; water comprises 90% by weight of the final composition; and the at least one other desirable ingredient comprises a total of 5% of the final composition.

8. The water-based lubricant of claim 5 wherein the at least one other desirable ingredient is triethanolamine.

9. A method of metalworking comprising the step of

utilizing a water-based lubricant comprising

phthalate ester in an amount of about 2% to about 20% based on the weight of the final composition;

water in an amount of about 60% to about 93% based on the weight of the final composition.

10. The method of claim 9 wherein the water-based lubricant further comprises at least one other desirable ingredient in a total amount of about 2% to about 20% based on the weight of the final composition.

AMENDED CLAIMS

[Received by the International Bureau on 01 February 2005 (01.02.2005); original claims 1, 3, 4, 5, 6, 9 and 10 amended, original claims 2, 7 and 8 unchanged (5 pages)]

+ Statement

1. A method of making a water-based lubricant composition comprising the steps of

providing water

providing a phthalate ester having at least one terminal hydroxyl group, wherein the phthalate ester is a reaction product that has been formed by

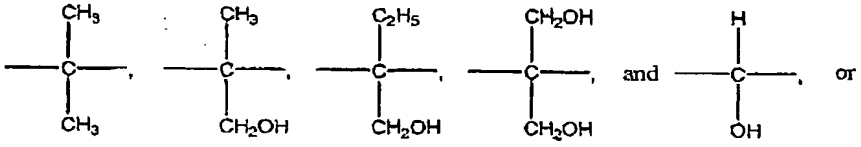
a. reacting phthalic anhydride with at least one alcohol, wherein the alcohol is either

(1) a fatty alcohol having the formula ROH, where R is C_4 to C_{22} branched or linear; or

(2) a polyol having the formula HO-R_1-OH, wherein R_1 represents:

(a) alkylene groups of 2 to 10 carbon atoms;

(b) -CH_2 -R_2 -CH_2- wherein R_2 represents:



(c) -$(R_3O)_n$-R_3-

where each R_3 independently is an alkylene group of 2 to 4 carbon atoms, and n is an integer of from 1 - 200; and

b. reacting the product resulting from the phthalic anhydride alcohol reaction with an alkoxylating agent to produce the phthalate ester reaction product having at least one terminal hydroxyl group; and

mixing the phthalate ester and water.

2. The method of claim 1 further comprising the steps of:

providing at least one other desirable ingredient; and

mixing the phthalate ester, water and at least one other desirable ingredient.

3. The method of claim 1 wherein the phthalate ester is provided in an amount of 2% to 20% based on the weight of the final composition; and

the water is provided in an amount of 60% to 93% based on the weight of the final composition.

4. The method of claim 2 wherein:

the phthalate ester is provided in an amount of 2% to 20% based on the weight of the final composition;

the water is provided in an amount of 60% to 93% based on the weight of the final composition; and

the at least one other desirable ingredient is provided in a total amount of 2% to 20% based on the weight of the final composition.

5. A water-based lubricant composition comprising:

water in an amount of 60% to 93% based on the weight of the final composition; and

phthalate ester in an amount of 2% to 20% based on the weight of the final composition, wherein the phthalate ester has at least one terminal hydroxyl group and is a reaction product that has been formed by

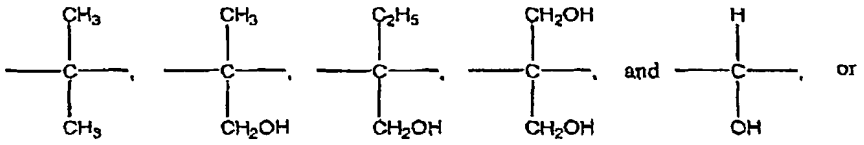
a. reacting phthalic anhydride with at least one alcohol, wherein the alcohol is either:

(1) a fatty alcohol having the formula ROH, where R is C_4 to C_{22} branched or linear; or

(2) a polyol having the formula HO-R_1-OH, wherein R_1 represents:

(a) alkylene groups of 2 to 10 carbon atoms;

(b) -CH_2 -R_2 -CH_2– wherein R_2 represents:



(c) -$(R_3O)_n$-R_3-

where each R_3 independently is an alkylene group of 2 to 4 carbon atoms, and n is an integer of from 1 - 200; and

b. reacting the product resulting from the phthalic anhydride alcohol reaction with an alkoxylating agent to produce the phthalate ester reaction product having at least one terminal hydroxyl group.

6. The water-based lubricant of claim 5 further comprising:

at least one other desirable ingredient in a total amount of 2% to 20% based on the weight of the final composition.

7. The water-based lubricant of claim 6 wherein the phthalate ester comprises 5% by weight of the final composition; water comprises 90% by weight of the final composition; and the at least one other desirable ingredient comprises a total of 5% of the final composition.

8. The water-based lubricant of claim 5 wherein the at least one other desirable ingredient is triethanolamine.

9. A method of metalworking comprising the step of:

utilizing a water-based lubricant composition comprising:

water in an amount of 60% to 93% based on the weight of the final composition;

a phthalate ester in an amount of 2% to 20% based on the weight of the final composition wherein the phthalate ester has at least one terminal hydroxyl group and is a reaction product that has been formed by

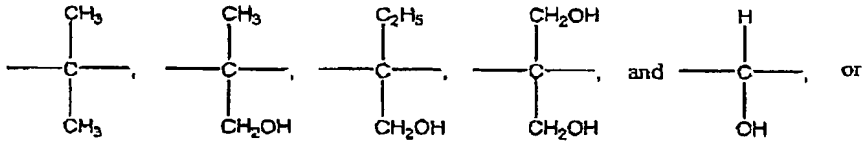
a. reacting phthalic anhydride with at least one alcohol, wherein the alcohol is either:

(1) a fatty alcohol having the formula ROH, where R is C_4 to C_{22} branched or linear; or

(2) a polyol having the formula HO-R_1-OH, wherein R_1 represents:

(a) alkylene groups of 2 to 10 carbon atoms;

(b) -CH_2 -R_2 -CH_2- wherein R_2 represents:



(c) -$(R_3O)_n$-R_3-

where each R_3 independently is an alkylene group of 2 to 4 carbon atoms, and n is an integer of from 1 - 200; and

b. reacting the product resulting from the phthalic anhydride alcohol reaction with an alkoxylating agent to produce the phthalate ester reaction product having at least one terminal hydroxyl group.

10. The method of claim 9 wherein, the water-based lubricant further comprises at least one other desirable ingredient in a total amount of 2% to 20% based on the weight of the final composition.

STATEMENT PURSUANT TO ARTICLE 19(1)/Rule 46

The International Bureau of the WIPO
34, Chemin des Colombettes
1211 Geneva 20, Switzerland

Dear Sirs:

The Applicant for the above-identified international application respectfully requests entry of the amendments described herein and embodied in the attached substitute sheets, pursuant to PCT Article 19 and Rule 46.

The amendment requested is the substitution of application pages 8-12 filed herewith for application pages 9-10, as originally filed. The substitution pages contain amended claims 1, 3, 4, 5, 6, 9 and 10, and original claims 2, 7 and 8. This letter and amendment are being transmitted by facsimile.

This amendment is being timely filed within 2 months from the date of transmittal of the International Search Report, which was mailed on December 1, 2004.

The amended claims all find support throughout the application as originally filed. Thus, the amendments do not go beyond the disclosure of the application as filed. Support for the amendments to claims 1, 5 and 9 may be found, for example, at pp. 2-3 of the amended application specification filed on July 13, 2004. The amendments made to claims 3, 4, 6 and 10 are for purposes of clarity.

The amendments to the claims are as follows:

INTERNATIONAL SEARCH REPORT

Inten [redacted] Application No
PCT/[redacted]03/38735

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10M173/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 402 839 A (PIOTROWSKI ALFRED B ET AL) 6 September 1983 (1983-09-06) * table 1, examples B,C *	1-10
X	US 2 959 547 A (BRILLHART DONALD D) 8 November 1960 (1960-11-08) * column 1, lines 64 to column 2, line 33* * examples 7,13,14 * * column 5, lines 28-36 * * example 17 * * column 6, lines 9-16 *	1-10
X	US 4 405 471 A (BERGVALL GOERAN A ET AL) 20 September 1983 (1983-09-20) examples 1,8,11	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 November 2004	01/12/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Perakis, N

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter[redacted]ation No
PCT/US [redacted]38735

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